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CONDITIONS ON THE OXIDATION OF TITANIUM

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ON THE OXIDATION OF TITANIUM

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Abstract

Multiwall is a new thermal protection system concept for advanced space transportation vehicles. The system consists of discrete panels made up of multiple layers of foil gage metal. Titanium is the proposed candidate metal for multiwall panels in the re-entry temperature range upto 675°C. Oxidation and embrittlement are the principal concerns related to the use of Ti in heat shield applications. This paper describes the results of a broad study on the oxidation kinetics of several titanium alloys subjected to different exposure conditions. The alloys include commercially-pure titanium, Ti-6Al-4V, and Ti-6Al-2Sn-4Zr-2Mo. Oxidation studies were performed on these alloys exposed at 704 °C in 5-760 torr air pressure and 0-50% relative humidity. The resulting weight gains were correlated with oxide thickness and substrate contamination. The contamination depth and weight gains due to solid solutioning were obtained from microhardness depth profiles and hardness versus weight percent oxygen calibration data.

## Introduction

Reusable thermal protection systems for hypervelocity vehicles have been the subject of research and development for over 20 years. These thermal protection systems (TPS) include the Reusable Surface Insulation (RSI) currently used on the space shuttle (1), metallic stand-off TPS(2), and multiwall (3-5). A design assessment of these three systems for space transportation vehicle heat shield applications indicates that the metallic TPS can be weight competitive (6). Titanium has been proposed for use in TPS applications at temperatures up to 675 °C (1250 °F). One of the potential problems with the use of titanium stems from its reactivity with oxygen at elevated temperatures (7-15). Such a reaction could be very detrimental since oxygen not only forms oxides at the surface but also penetrates the metal lattice, in which it is extremely soluble, causing embrittlement.

This paper presents the results from a study of the kinetics of oxidation and diffusion in three titanium alloys: commercial purity titanium (Ti-A55), Ti-6Al-4V (Ti-6-4), and Ti-6Al-2Sn-4Zr-2Mo (Ti-6-2-4-2). The Ti-A55 provides a reference single-phase material; Ti-6-4 represents the most common aerospace alloy of titanium; and Ti-6-2-4-2 is a prime candidate alloy for TPS applications. These alloys (in sheet and/or foil form) were exposed to 704°C (1300°F) at 5 or 760 torr air pressure and at a room-temperature relative-humidity (RH) of 0% or 50%. The 5 torr pressure and 0% humidity represent approximate air pressure and humidity at peak temperature for a re-entry trajectory. The air-contaminated specimens were analyzed for weight-gains due to oxide growth and oxygen penetration.

## Nomenclature

AC	acid cleaned
AC*	acid cleaned thoroughly to remove appreciable surface material
AR	as-received
Atm	air at 760 torr
$c_s$	solid solubility of oxygen at the oxide/metal interface, weight % oxygen
Dry	air with ~0% RH
KHN	Knoop hardness number
LID	liquid interface diffusion heat treatment cycle
Lpr	air at 5 torr
MP	multiparameter (temp., load, and air-pressure) test system
PM	powder metallurgy
RH	room-temperature relative humidity, percent
TGA	thermogravimetric analysis
Ti-A55	commercial purity titanium with yield strength of 55 ksi
Ti-6-2-4-2	Ti-6Al-2Sn-4Zr-2Mo alloy
Ti-6-4	Ti-6Al-4V alloy
VA	vacuum annealed
Wet	air with ~50% RH
$w_f$	$w_s/w_t$
$w_s$	weight-gain rate due to solid solubility of oxygen, $\mu\text{g cm}^{-2} \text{ hr}^{-1/2}$
$w_t$	total weight-gain rate ( $= w_s + w_\xi$ ), $\mu\text{g cm}^{-2} \text{ hr}^{-1/2}$
$w_\xi$	weight-gain rate due to oxide formation, $\mu\text{g cm}^{-2} \text{ hr}^{-1/2}$
$\xi$	oxide thickness, $\mu\text{m}$

## Review of Literature

Titanium reacts with oxygen and nitrogen at elevated temperatures. Although the absorption of nitrogen by titanium is generally similar to that of oxygen in that both processes are substantially independent of gas pressure (7), the rate of absorption of nitrogen is much less rapid than the rate of absorption of oxygen. In fact, nitrogen plays only a minor role in the scaling of titanium in air because of the instability of titanium nitride with respect to titanium oxides, and the lower diffusion rate of nitrogen in titanium (7).

## Oxidation Rates

The scale formed on the surface of titanium has been studied by a number of researchers, all of whom reported that the scale consists of  $TiO_2$  in the form of rutile. Jenkins (8) examined the physical nature of the oxide scales formed on titanium in an oxygen atmosphere at 700 torr pressure. He concluded that the oxidation process in titanium depends on the reaction between oxygen and titanium occurring at the metal/oxide interface, i.e., it is oxygen and not titanium which diffuses through the scale. He based this conclusion on the fact that fiducial marks made on the surface of the metal before oxidation appeared on the outer surface of the scale and that, on re-absorption of the adherent scale brought about by vacuum annealing for sufficient time, the markings could again be observed on the metal surface. Jenkins suggested that there are three stages in the oxidation process which occur under different time-temperature conditions. The first stage involves the formation of a thin layer of dense scale through which the movement of oxygen is by a process of anion-vacancy diffusion giving rise to a parabolic oxidation rate. In the second stage (observed in the exposure range of 72 hours at  $740^\circ C$  to 12 hours at  $840^\circ C$ ), the scale becomes sufficiently thick to break up and become porous, thus greatly facilitating the access of oxygen to the metal surface and a linear oxidation rate results. In the third stage (especially at high temperatures) sintering of the porous scale might result, thereby imposing a continuous barrier between the free oxygen and the metal surface. The oxidation rate becomes diffusion-dependent once more, thus bringing about a reversion to a parabolic oxidation law. Changes of this kind occurring with both time and temperature could account for the observed disagreements in overall oxidation rates between the findings of various researchers.

## Substrate Contamination

Although the thickness of surface oxide formed is controlled by diffusion of oxygen through  $TiO_2$ , the extent to which the underlying metal is contaminated is dependent on the rate of diffusion of oxygen through the metal. At the present time there is no theoretical basis for believing that any appreciable reduction in this diffusion rate can be brought about by simple alloying. A comparison of the air-contamination rate data below  $820^\circ C$  ( $1500^\circ F$ ) for Ti-A55, Ti-6-2-4-2 and several other alloys of titanium shows that titanium alloys with higher substitutional alloying content have higher rates of diffusion (9). Most of the titanium alloys, excluding Ti-A55, vary within a factor of two in depth of contamination for given oxidizing conditions (9).

### Effect of Oxygen Pressure

Studies on the kinetics of oxygen absorption on titanium surface at different oxygen partial pressures, clearly indicate that the rate of oxygen absorption is not proportional to the square root of the oxygen pressure. This means that surface absorption is not the rate-controlling factor in the scaling (oxide formation plus matrix contamination) of Ti. Hurlen (10) studied the oxidation kinetics of Ti at 400-700°C (~750-1300°F) and 0.01-760 torr oxygen pressures. His weight gain data for 16 hours at 540-700°C (~1000-1300°F) indicate that at these temperatures the oxidation is virtually independent of oxygen pressure in the range 1-760 torr. Below 540°C, the oxidation rate is maximum at 760 torr and minimum at about 10 torr.

### Summary of Review

The literature on titanium oxidation over the last thirty years has been quite extensive (7-15). However, there are a few issues on which the literature is scanty or nonexistent. These pertain to: (1) the surface cleanliness of the alloy and its effect on the oxidation kinetics; (2) the effect of air pressure and humidity on the oxidation rates; (3) whether or not microstructural differences significantly affect oxidation kinetics in commercial alloys; (4) the oxygen partitioning between the two basic components of oxidation, namely oxide growth and matrix contamination. The present investigation addresses these issues.

### Experimental Details

#### Materials

The alloys used are: (a) 3.08 mm thick Ti-A55 sheet, (b) 0.05 mm thick Ti-A55 foil, (c) 0.62 mm thick Ti-6-2-4-2 sheet, (d) 0.08 mm thick Ti-6-2-4-2 foil, (e) 0.12 mm thick Ti-6-2-4-2 PM foil, (f) 0.89 mm thick Ti-6-4 sheet, and (g) 0.08 mm thick Ti-6-4 foil. The chemical composition for five of these alloys is given in Table I. The alloys (e) and (f) can be assumed to have compositions similar to those of (d) and (g), respectively. All the alloys had a combined base level of oxygen plus nitrogen of about 0.13 wt% with the exception of Ti-6-4 which had 0.27 wt%.

Table I. Chemical Composition of the Various Titanium Alloys

Element Alloy	Al	Sn	Zr	Mo	V	Fe	Si	H	C	N	O	OET *	Ti
Ti-A55 Sheet	-	-	-	-	-	.08	-	.01	.02	.01	.14	<.4	Bal
Ti-A55 Foil	-	-	-	-	-	.19	-	-	.02	.03	.10	<.4	Bal
Ti-6-2-4-2 Sheet	6.05	1.94	3.80	2.00	-	.04	.06	.02	.02	.01	.13	<.3	Bal
Ti-6-2-4-2 Foil	5.80	1.87	4.00	2.06	-	.20	.06	.05	.02	.01	.12	<.4	Bal
Ti-6-4 Foil	5.74	-	-	-	4.18	.15	-	.01	.02	.04	.23	<.4	Bal

\*OET = Other Elements Total.

### Exposure Apparatus

The oxidation experiments were performed using a thermogravimetric analysis unit (TGA) and the NASA Langley Multi-Parameter Test System (MP) (16). The TGA unit consisted of a vertical tube furnace, a Cahn-Ventron electrobalance for continuous monitoring of specimen weight, and a micro-computer for data collection. The MP test system consisted of a vertical furnace with Pt or nichrome heating elements and a vacuum system. Air was bled in to provide desired air pressure and relative humidity. Whereas the TGA provided continuous weight-gain data, the MP test system gave only total weight gain at the end of exposure.

### Specimen Details

The Ti-A55 specimens were nominally 15 mm x 15 mm, and all other specimens were nominally 15 mm x 10 mm. All the specimens were cleaned with soap solution followed by ultrasonic agitation in acetone. Certain specimens were acid cleaned (AC) in a Kroll's solution (3% HNO<sub>3</sub> + 2% HF) for 15 seconds to give a bright, shiny surface. The designation "AC\*" refers to rigorous acid cleaning involving appreciable material removal. A few of the Ti-A55 and Ti-6-2-4-2 specimens were vacuum annealed (VA) at 870°C (≈1600°F) for 100 hours at  $\approx 7 \times 10^{-7}$  torr in order to coarsen their grain structure.

Certain specimens were acid cleaned, and were subjected to an argon environment at 927°C (≈1700°F) for approximately 2.5 hours. This heat treatment cycle is identical to the thermal cycle employed in the liquid-interface-diffusion (LID) braze process which is used in fabricating titanium multiwall TPS panels. The acid cleaning together with the above heat treatment cycle will be referred to as the LID condition.

### Exposure Conditions

All exposures were conducted at 704°C (1300°F) for 24 hours. This condition was selected because it was severe enough to assure weight changes large enough to be measured accurately, but not so severe that it produced linear oxide growth. Further, calculations similar to those outlined in reference 13 show that the 24-hour exposure at 704°C is equivalent to about 420 space shuttle missions with a peak temperature of 675°C (1250°F).

The TGA experiments were performed using laboratory air (760 torr pressure and ≈50% RH). The MP experiments were performed using dry air (2 ppm water vapor) or ≈50% RH air at a pressure of 5 or 760 torr.

### Ti(O) Standards

In order to obtain oxygen concentration profiles from microhardness depth profiles, Ti(O) standards were prepared in the following manner. Several specimens of Ti-A55 and Ti-6-2-4-2 foils were oxidized in air for different lengths of time at 855°C (≈1570°F) to pick up different amounts of oxygen. These were subsequently vacuum annealed at 870°C (≈1600°F) for 120 hours in a vacuum of better than  $7 \times 10^{-7}$  torr. The vacuum annealing exposures increased the specimen weights only slightly (0.05 to 0.40%), indicating an acceptable vacuum level. Therefore, concentration gradients were expected to be minimal.

The above standards were analyzed by electron microprobe for surface composition. Special standardization and data reduction schemes were used so that the oxygen weight percent in a specimen was determined by using metal(s) k-ratio alone. The resulting compositions were in excellent agreement with weight %  $O_2$  at the end of vacuum annealing. Alpha-phase microhardness was obtained on these specimens. At least 15 microhardness impressions were made on each specimen. The cross sections did not reveal any trace of  $TiO_2$ . Thus the weight %  $O_2$  at the end of vacuum annealing represents the oxygen content in solid solution.

#### Metallography

The cross sections of sheet and foil specimens, in the as-received and exposed conditions, were conventionally prepared for metallography using Kroll's reagent (2%  $HNO_3$  + 1%  $HF$ ). The exposed specimens were copper-coated prior to metallographic preparation, in order to preserve the surface oxide. Microhardness depth profiles were obtained for the cross sections of exposed specimens, employing a 15 g load and a Knoop indenter. The optics in the microhardness tester enabled the measurement of the long diagonal of the hardness impressions and also the oxide thickness to 0.1  $\mu m$ . The exposed specimens were studied using a scanning electron microscope to reveal differences, if any, in the morphology of oxide growth as affected by alloy chemistry and exposure conditions.

### Results and Discussion

#### Air Contamination

Titanium air-contamination studies and subsequent modeling are typically based on weight gain data, microhardness measurements and lattice parameter determination. Based on the absence of titanium nitrides in air-contaminated specimens, it is always assumed that only oxygen diffuses into the specimen. However, since both O and N are interstitial atoms, hardness and lattice parameter changes cannot distinguish between these elements. An attempt was made in the present investigation to verify the absence (or presence) of nitrogen by using electron microprobe. Although  $NK_\alpha$  and  $TiL_1$  lines are close to each other, it was demonstrated by using BN and pure Ti standards that these lines are clearly resolvable on a wavelength scan. Titanium specimens containing different levels of oxygen (13% and 2%) were prepared by partial oxidation in air and subsequent high temperature homogenization in vacuum. When these specimens were subjected to a wavelength scan, it was clearly evident that they contained no detectable nitrogen. Thus it was concluded that when Ti is exposed to air at elevated temperatures, only oxygen reacts with the metal.

#### Weight-Gain Data

Figure 1 shows weight-gain as a function of time for the acid cleaned Ti-A55 sheet specimen subjected to TGA at 704°C. It typically takes about 35-40 minutes to reach 704°C and the equivalent time for this rise cycle is virtually zero when compared to the total exposure time at 704°C. This was taken into consideration by modifying the instantaneous time so that it represents effective time at 704°C. Also it takes about an hour for the buoyancy effects to subside. Therefore the true weight gain rate is the slope of the curve from 1 hour exposure onwards, and this is about

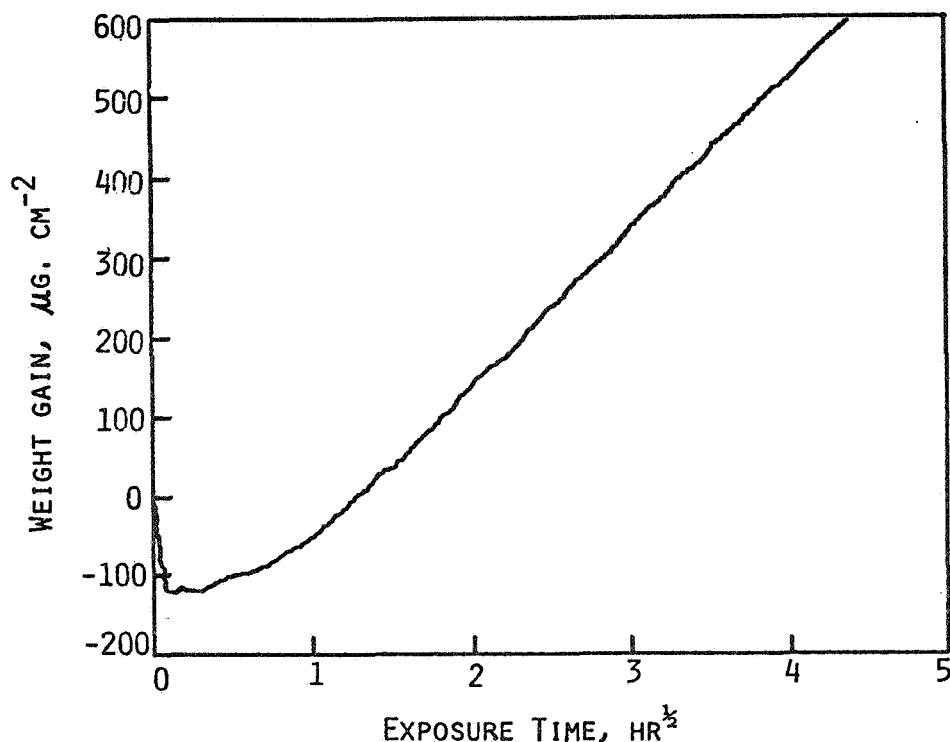


Figure 1 - TGA data of acid-cleaned Ti-A55 sheet exposed at 704°C.

198  $\mu\text{g cm}^{-2} \text{ hr}^{-1/2}$ . This value is in good agreement with Morton and Baldwin's value of 180 (11).

The weight-gain data for all the specimens exposed in TGA indicate similar effects in that all the weight-gains are parabolic in nature (i.e., weight gain is proportional to square root of time, or weight gain squared is proportional to time). The weight-gain rates for Ti-A55 are shown in Table II, for Ti-6-2-4-2 in Table III, and for Ti-6-4 in Table IV. These are summarized in Table V. The TGA data are expected to agree with the MP Atm-Wet data. However, they are slightly lower (Table V) probably due to insufficient airflow and the associated blanketing effect in the TGA case.

#### Surface Cleanliness

The overall oxidation kinetics of titanium alloys are dependent on the original condition of the alloys. The original condition here refers to the cleanliness of the sheet or the foil specimens prior to the oxidation exposure. Failure to recognize the importance of cleanliness of the alloys results in an extra variable that may affect the results on oxidation for supposedly the same basic composition and microstructure. Cleanliness may be critically viewed as the condition specifying the presence or absence of an oxide layer on the alloy specimens as a result of thermo-mechanical processing typical of fabrication. For example, a foil, by virtue of its considerable reduction in section thickness is expected to contain more oxygen and hence be "dirtier" than a sheet of the same basic composition. In addition,  $\approx 0.1 \mu\text{m}$  thick surface oxide layer is expected to be a part of the makeup of the alloys in the as-received condition. These two basic



Table II. Weight-Gain Rates for Ti-A55 Sheet Exposed at 704°C in Air

Material Condition	Specimen Thickness, mm	Exposure Conditions	Facility	Specimen #	$\mu\text{g cm}^{-2} \text{ hr}^{-1/2}$	
						Average
AR	3.09	Lab Air	TGA	SPC 09	175	170
	3.08			SPC 17	166	
	3.08			SPC 22	168	
AC	3.08	Lab Air	TGA	SPC 03	197	195
	3.09			SPC 04	196	
	3.08			SPC 23	190	
AC*	2.97			SPC 24	198	
AC-VA	3.09	Lab Air	TGA	SPC 10	201	200
	AC-VA-AC*			SPC 25	199	
VA-AC	3.08	Lab Air	TGA	EXP 23	191	175
	3.08			EXP 51	172	
	3.08			EXP 53	158	
	3.08			EXP 54	199	
	3.08			EXP 55	157	
AC	3.08	Lpr - Dry	MP	A17, A18, A19	142	139
	3.08			A20, A21, A22	133	
	3.08			A23, A24, A25	143	
AC	3.08	Atm - Wet	MP	A26, A27, A28, A29	218	223
	3.08			A30, A31, A32, A33	227	
AC	3.08	Atm - Dry	MP	A34, A35, A36, A37	201	197
	3.08			A42, A43, A44, A45	198	
	3.08			A46, A47, A48, A49	193	
VA-AC	3.08	Lpr - Dry	MP	A14	120	120
VA-AC	3.08	Atm - Dry	MP	A03	182	182

Note: AC\* denotes that the specimen has been acid cleaned rigorously.

Table III. Weight-Gain Rates for Ti-6-2-4-2 Exposed at 704°C in Air

Material Condition		Specimen Thickness, mm	Exposure Conditions	Facility	Specimen #	Wt, $\mu\text{g cm}^{-2} \text{ hr}^{-1/2}$	
							Average
S H E E T	AR	0.60 0.60 0.63 0.63 0.62 0.61	Lab Air	TGA	EXP 82 EXP 84 SPC 13 SPC 15 SPC 12 SPC 14	53 52 61 60 50 51	55
	AC*	0.58	Lab Air	TGA	SPC 26	60	60
	VA-AC*	0.58 0.58	Lab Air	TGA	EXP 32 EXP 70	52 50	51
	AC-VA-AC*	0.52	Lab Air	TGA	SPC 16	57	57
	VA-AC	0.62	Atm - Dry	MP	B04	65	65
	VA-AC	0.62	Lpr - Dry	MP	B01, B05, B09	65	65
	AC	0.62	Lpr - Dry	MP	B19, B20, B21	66	66
	AC	0.62 0.62	Atm - Dry	MP	B54, B46, B47, B48 B49, B50, B51, B52	80 76	78
F O I L	AC	0.62 0.62	Atm - Wet	MP	B37, B38, B39, B40 B41, B42, B43, B44	76 76	76
	AR	0.08 0.08	Lab Air	TGA	SPC 08 SPC 20	52 52	52
	AC	0.07 0.06	Lab Air	TGA	SPC 01 SPC 06	63 58	61
	LID	0.08 0.08	Lab Air	TGA	SPC 02 EXP 96	58 66	62
	AR PM	0.12 0.13 0.11	Lab Air	TGA	EXP 46 EXP 79 EXP 98	82 80 74	79
	AC PM	0.09	Lab Air	TGA	SPC 27	87	87

Table IV. Weight-Gain Rates for Ti-6-4 Exposed at 704°C in Air

Material Condition	Specimen Thickness, mm	Exposure Conditions	Facility	Specimen #	$w_t$ , $\mu\text{g cm}^{-2} \text{hr}^{-1/2}$	
						Average
LID Sheet	0.89	Lab Air	TGA	EXP 80	244	245
	0.89			EXP 83	264	
	0.89			EXP 85	223	
	0.89			EXP 89	258	
	0.89			EXP 91	234	
LID Foil	0.08	Lab Air	TGA	EXP 78	230	229
	0.08			EXP 81	224	
	0.08			SPC 05	232	
LID Foil	0.08	Lpr - Dry	MP	C02,C03	156	156
	0.08			C05,C06,C07	155	
LID Foil	0.08	Atm - Dry	MP	C11,C12,C13	228	231
	0.08			C14,C15,C16	233	
LID Foil	0.08	Atm - Wet	MP	C21,C23,C22	250	240
	0.08			C31,C27,C26	241	
	0.08			C30,C24,C28	228	

Table V. Summary of Weight-Gain Rates ( $w_t$ ,  $\mu\text{g cm}^{-2} \text{hr}^{-1/2}$ ) at 704°C

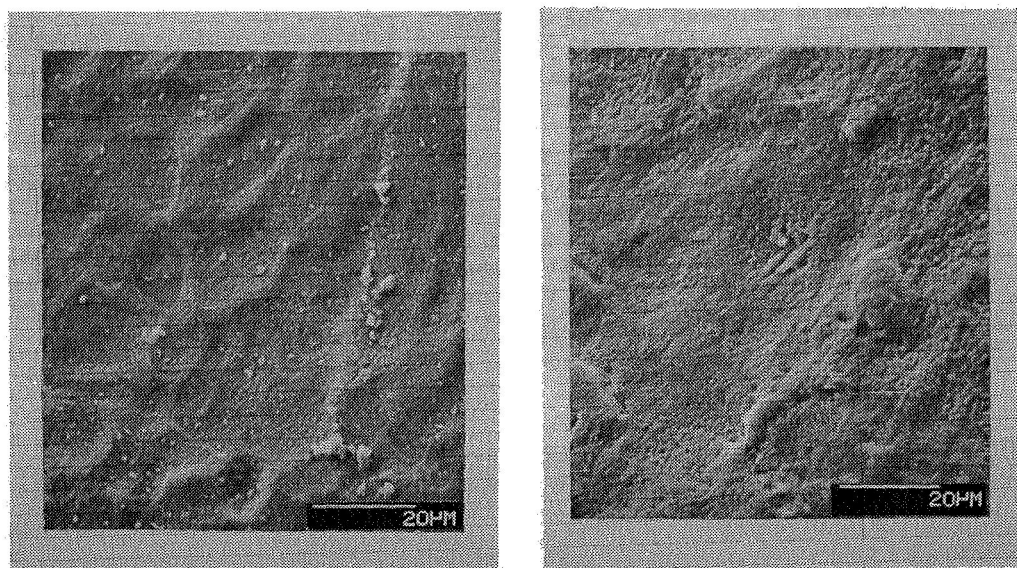
Material Condition	TGA Lab Air	MP		
		Atm-Wet	Atm-Dry	Lpr-Dry
Ti-A55 AR Sheet	170	-	-	-
Ti-A55 AC Sheet	195	223	197	139
Ti-A55 VA-AC Sheet	175	-	182	120
Ti-A55 AC-VA-AC* Sheet	200	-	-	-
Ti-6-2-4-2 AR Sheet	55	-	-	-
Ti-6-2-4-2 AC Sheet	60	76	78	66
Ti-6-2-4-2 VA-AC Sheet	51	-	65	65
Ti-6-2-4-2 AC-VA-AC* Sheet	57	-	-	-
Ti-6-2-4-2 AR Foil	52	-	-	-
Ti-6-2-4-2 AC Foil	61	-	-	-
Ti-6-2-4-2 LID Foil	62	-	-	-
Ti-6-2-4-2 AR PM Foil	79	-	-	-
Ti-6-2-4-2 AC PM Foil	87	-	-	-
Ti-6-4 LID Sheet	245	-	-	-
Ti-6-4 LID Foil	229	240	231	156

components of "dirt" can appreciably affect the intake of oxygen during an exposure and may very well account for the scatter in the literature data on titanium oxidation. It is for this reason that the various alloys in the present investigation were subjected to acid cleaning in a Kroll's solution. AC and AC\* refer to acid cleaning. While AC represents mild acid cleaning with minimal material removal, AC\* represents vigorous acid cleaning involving significant material removal. AC\* would then be expected to wholly remove the surface oxide layer.

Table V contains data on the effect of surface cleanliness. For Ti-A55, the  $w_t$  increased from 170 for as-received (dirty) condition to 195 for acid cleaned condition. For Ti-6-2-4-2 the  $w_t$  increased from 55 to 60 for the sheet, 52 to 61 for the foil, and 79 to 87 for the PM foil. Thus surface cleanliness has a 9-17% effect on the oxidation rate. This clearly demonstrates the need to acid clean the as-received alloys prior to an oxidation exposure, so that cleanliness is not a factor affecting the kinetics.

When the as-received Ti-A55 specimen was vacuum annealed without prior acid cleaning, the thin oxide might have been expected to dissolve into the base metal. The resulting VA-AC specimen showed a  $w_t$  value of 175 which is nearly the same as that for the AR condition.

Air Pressure.— The effect of air pressure is significant as can be seen from the Atm-Dry versus Lpr-Dry data of Table V. The 5 torr exposure (Lpr) results in a decrease in oxidation rate (with respect to 760 torr) of about 29% for Ti-A55 AC sheet, 15% for Ti-6-2-4-2 AC sheet, and 32% for Ti-6-4 LID foil. This is because the reduced oxygen quantity at 5 torr results, as will be seen later, in a lower oxide thickness and  $c_s$ . Also, the oxide after 5 torr exposure appears to be less uniform in thickness than after the 760 torr exposure (Fig. 2).



(a) 5 torr

(b) 760 torr

Figure 2 - SEM surface-micrographs of Ti-A55 sheet exposed at 704°C for 24 hours in dry air at 5 or 760 torr.

Air Humidity.— The effect of humidity can be seen from the Atm-Wet versus Atm-Dry data of Table V. The 0% RH exposure (Dry) results in a decrease in oxidation rate (with respect to 50% RH air) of about 12% for Ti-A55 AC sheet, and 4% for Ti-6-4 LID foil. The rates for Ti-6-2-4-2 AC sheet are approximately equal.

#### Grain-Size and Microstructural Effects

The Ti-A55 sheet had a grain size of  $\approx 20 \mu\text{m}$  in the AR or AC condition. To determine whether grain size had a significant influence on oxidation, a few Ti-A55 specimens were subjected to a 100-hour anneal at  $870^\circ\text{C}$  ( $1600^\circ\text{F}$ ) in a vacuum ( $\approx 7 \times 10^{-7}$  torr). This heat treatment (VA) resulted in a grain size of  $\approx 130 \mu\text{m}$ . To ensure that the VA specimens had no surface oxide layer, which could mask the influence of the coarse  $\alpha$ -grains underneath, it was subjected to thorough acid cleaning. The resulting specimen (AC-VA-AC\*) gave a value of 200 for  $w_t$  (Table V). This value when compared to  $w_t = 195$  for the AC condition clearly indicates that grain size in the range investigated has no discernible influence on the oxidation of Ti-A55 at  $704^\circ\text{C}$ .

The Ti-6-2-4-2 in the AR condition had a two-phase microstructure with  $\alpha$ -grain size of  $\approx 15 \mu\text{m}$  and  $\approx 10 \mu\text{m}$  for sheet and foil, respectively. The VA treatment did not appreciably alter the grain sizes and the resulting oxidation behavior was similar to that of sheet without VA treatment. The AC-sheet and AC-foil specimens have about the same oxidation rates indicating that the minor variations in microstructure that were discernible in the foil and sheet do not affect the oxidation kinetics.

The Ti-6-2-4-2 PM foil showed a significantly higher weight-gain rate than the regular foil (79 versus 52). This may be ascribed to the presence of interconnected pores, typical of powder metallurgy products, which significantly increase the net internal surfaces and hence the oxidation rate. The cross-section of Ti-6-2-4-2 PM foil revealed rather large elongated grains of  $\alpha$  (grain size  $\approx 30 \mu\text{m}$ ) and  $\beta'$ . Some of the  $\alpha$ -grains contained pores inside them or at their grain boundaries.

Ti-6-4 sheet in the AR condition revealed a dual phase microstructure of equiaxed  $\alpha$  and  $\beta$  with  $\approx 10 \mu\text{m}$   $\alpha$ -grain size. The foil on the other hand showed a fine distribution of  $\alpha$  and  $\beta$  with an  $\alpha$ -grain size of  $\approx 5 \mu\text{m}$ . The nominally lower  $w_t$  value for foil (Table V) may be ascribed to the foil being "dirtier" than the sheet, in view of its fabrication history involving larger reductions in thickness. The influence of microstructure on oxidation would be marginal as was evident for Ti-6-2-4-2.

#### Partitioning of Oxygen

Figures 3, 4, and 5 show microhardness depth profiles for Ti-A55, Ti-6-2-4-2, and Ti-6-4 exposed at  $704^\circ\text{C}$  ( $1300^\circ\text{F}$ ) for 24 hours. Oxygen concentration profiles were derived from the microhardness depth profiles using the KHN versus weight % O data shown in Tables VI and VII for Ti-A55 and Ti-6-2-4-2. (In view of its similarity in chemistry, the Ti-6-2-4-2 data were also used for Ti-6-4.) The resulting oxygen depth profiles are shown as insets in Figures 3, 4, and 5. The weight-gain rate due to matrix contamination ( $w_g$ ) was computed from the area under each of these oxygen profiles. The weight-gain rate due to oxide growth ( $w_\xi$ ) was computed from the oxide thickness ( $\xi$ ) measurements. These  $\xi$ ,  $w_\xi$ , and  $w_g$  values are shown in Table VIII for the different alloys investigated. The  $w_t$  in Table VIII

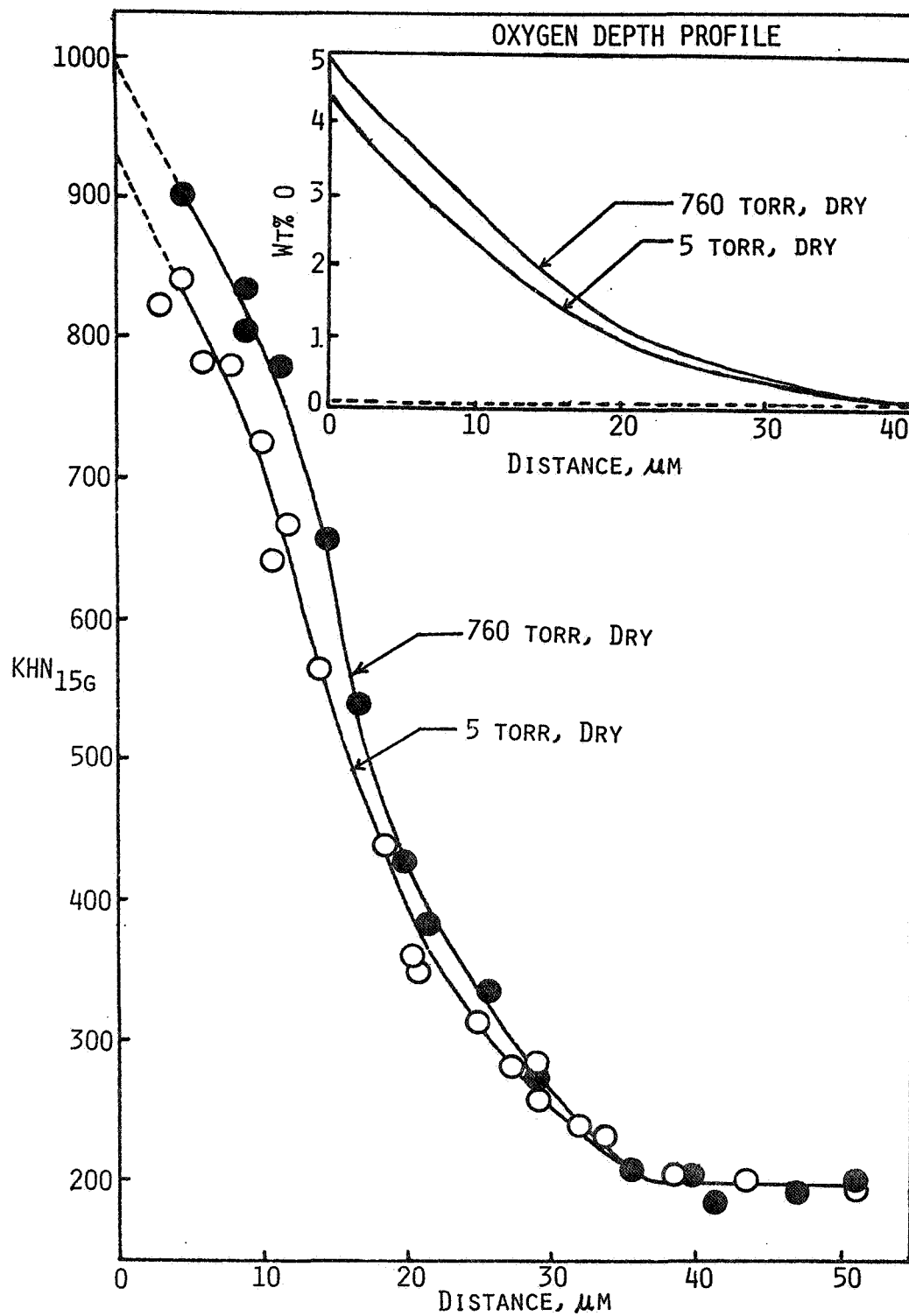


Figure 3 - Microhardness/oxygen depth-profiles in Ti-A55 sheet exposed at 704°C for 24 hours in dry air at 5 or 760 torr.

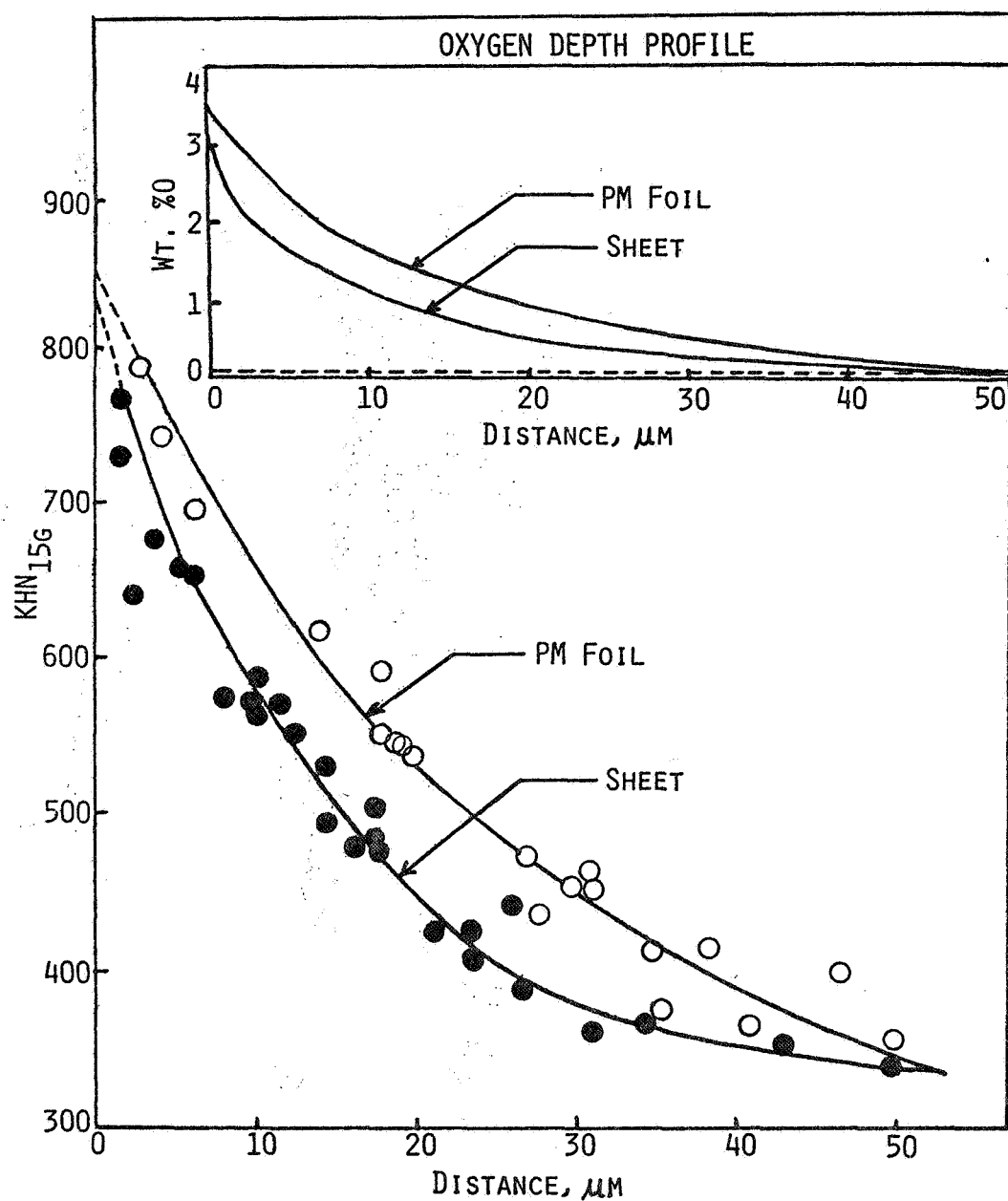


Figure 4 - Microhardness/oxygen depth-profiles in Ti-6-2-4-2 sheet and PM-foil exposed at 704°C for 24 hours in laboratory air.

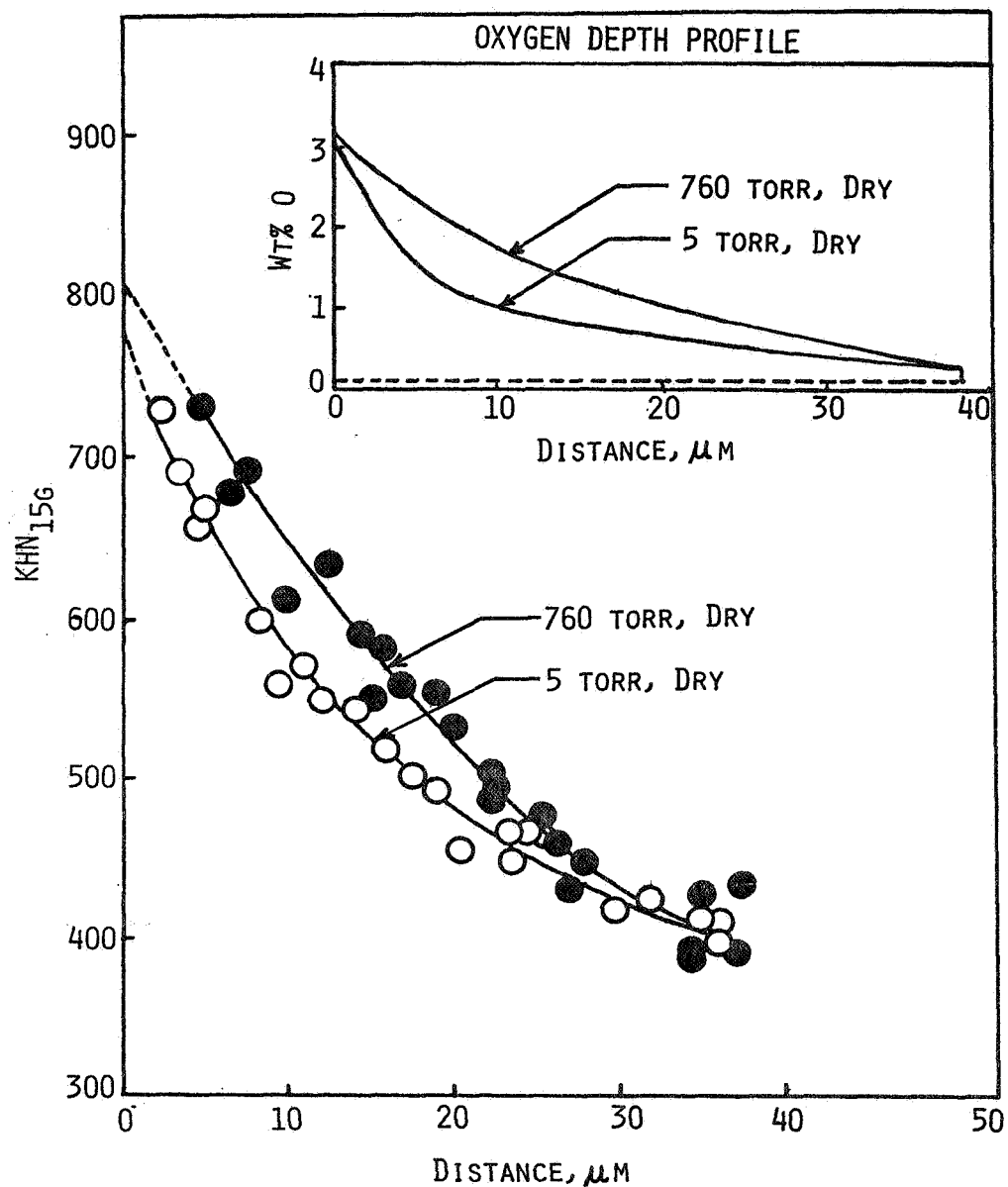


Figure 5 - Microhardness/oxygen depth-profiles in Ti-6-4 foil exposed at 704°C for 24 hours in dry air at 5 or 760 torr.



Table VI. Hardness Versus Percent-Oxygen Data for Ti-A55

KHN-15g	180	650	860	900	1085	1530	1570
Wt. % O	0.15	2.01	3.13	3.89	5.83	10.80	12.78

Table VII. Hardness Versus Percent-Oxygen Data for Ti-6-2-4-2

KHN-15g	355	410	474	521	574	734	812	934	1009	1123
Wt. % O	0.15	0.36	0.62	0.75	0.87	2.08	3.27	5.01	6.25	7.49

Table VIII. Weight-Gain Rates ( $\mu\text{g cm}^{-2} \text{ hr}^{-1/2}$ ) due to Solid Solubility and Oxide Formation for Specimens Exposed to 704°C for 24 Hours

Material Condition *	Exposure Conditions	Sp. #	$\xi$ $\mu\text{m}$	$w_{\xi}$	$w_B$	$(w_B + w_{\xi})$	$w_t$	$\frac{w_B}{w_t}$
Ti-A55 VA-AC Sheet	Atm - Dry	A03	$3.2 \pm .3$	111	61	172	182	0.34
	Lpr - Dry	A14	$1.9 \pm .2$	66	53	119	120	0.44
Ti-6-2-4-2 VA-AC Sheet	Atm - Dry	B04	$0.8 \pm .1$	28	25	53	65	0.38
Ti-6-2-4-2 PM Foil	Lab Air	EXP79	$1.0 \pm .3$	35	42	77	80	0.52
Ti-6-4 LID Foil	Atm - Dry	C14	$4.8 \pm .2$	167	40	207	233	0.17
	Lpr - Dry	C02	$4.3 \pm .3$	149	27	176	156	0.17

represents total weight-gain rate obtained independently from the initial and post-oxidation weights of the specimen. The excellent agreement between ( $w_{\xi} + w_s$ ) and  $w_t$  reflects the confidence level on the three independent measurements ( $w_{\xi}, w_s, w_t$ ). The following observations are made with reference to Figures 3, 4, and 5 and Table VIII.

**Solid Solubility of Oxygen.**— The solid solubilities of oxygen in the matrix at the oxide-metal interface,  $c_s$ , for the 704°C - 24 hours - 760 torr - dry air exposure are:  $\approx 5$  weight % O for Ti-A55,  $\approx 3$  weight % O for Ti-6-2-4-2, and  $\approx 3$  weight % O for Ti-6-4 (Figs. 3,4,5). Recognizing that the gradients would be steep at the oxide-metal interface, the true values of solid solubility (under the present conditions of exposure) would be slightly higher than those indicated above. In the literature, however, it is customarily assumed that  $c_s = 14.3$  (which is the maximum oxygen solid solubility in  $\alpha$ -Ti), regardless of temperature and time of exposure or the alloy chemistry. As a matter of fact, the equilibrium  $c_s$  is expected to be significantly lower than 14.3 for an alloy of Ti depending upon the alloying elements. In addition,  $c_s$  for any given alloy would be a function of temperature and time; the higher the temperature of exposure, the lower the time to attain the equilibrium  $c_s$ . It is therefore pertinent to estimate the correct value of  $c_s$  attained under a given exposure, since the extent of matrix contamination is directly proportional to the actual value of  $c_s$ .

**Matrix Contamination.**— The depth of contamination is defined as the distance into the metal, as measured from the oxide-metal interface, at which oxygen concentration reaches the base initial value (or equivalently the distance at which microhardness decreases to the base value of the uncontaminated alloy). The depths of contamination for 704°C - 24 hours - 760 torr - dry air exposure are: 37  $\mu\text{m}$  for Ti-A55, 40  $\mu\text{m}$  for Ti-6-2-4-2, and 43  $\mu\text{m}$  for Ti-6-4 (Figs. 3,4,5). Therefore, the average value for the three alloys investigated is about 40  $\mu\text{m}$ . Since oxygen in solution has an embrittling effect on the mechanical properties of titanium, the depth of contamination can be correlated with useful level of toughness in Ti-alloys (9). The depth of 40  $\mu\text{m}$  for Ti-6-2-4-2 in the present investigation is in excellent agreement with that found by Shamblen and Redden (9).

The depth of contamination being nearly the same for all the alloys investigated,  $w_s$  should be directly proportional to  $c_s$  if the diffusion coefficients are nearly same. This indeed is the case for Ti-6-4 and Ti-A55, as indicated by the  $w_s$  values of 40 and 61 respectively for the corresponding  $c_s$  values of 3 and 5 weight %.

**Oxide Growth.**— The  $w_{\xi}$  for Ti-6-4 is higher than that for Ti-A55 (167 versus 111, see Table VIII). The alloying elements in Ti-6-4 somehow modify the scale so as to increase the oxide growth. On the other hand, the presence of Zr and Sn in Ti-6-2-4-2 ( $w_{\xi} = 28$ ) drastically reduces the oxide growth. This fact is also highlighted by the  $\xi$  values of 3.2, 4.8, and 0.8  $\mu\text{m}$  respectively for Ti-A55, Ti-6-4 and Ti-6-2-4-2.

The fraction of oxygen partitioned into solid solution,  $w_f$ , may be represented by the ratio  $w_s/w_t$  (Table VIII). This ratio for the three alloys, exposed at 704°C for 24 hours in 760 torr dry air are: 0.17 for Ti-6-4, 0.34 for Ti-A55, and 0.38 for Ti-6-2-4-2. The values of  $w_f$  for Ti-6-4 and Ti-A55 are in the same ratio of 3:5 as are their  $c_s$  values. In this sense, Ti-6-4 and Ti-A55 are similar in their oxidation behavior. On the other hand,  $w_f$  for Ti-6-2-4-2 is high in spite of the fact that  $c_s$  for Ti-6-2-4-2 is only  $\approx 3$  weight %. This is simply because of the low contribution due to  $w_{\xi}$  and therefore  $w_t$ . Lopes (15) obtained a value of 0.29 for  $w_f$  in commercial purity Ti exposed at 750°C in pure oxygen atmosphere.

This is in good agreement with the value of 0.34 obtained in the present investigation.

#### Summary

The results of this investigation on the oxidation of Ti-A55, Ti-6-4, and Ti-6-2-4-2 exposed at 704°C (1300°F) for 24 hours in air at 5 or 760 torr and relative humidity of 0 or 50% are summarized as follows:

- (1) Surface cleanliness has a 9-17% effect on the oxidation rate; cleaner surfaces gain more weight.
- (2) The 5 torr exposure results in about 15-32% lower oxidation rate than the 760 torr exposure. The lower rate at 5 torr is due to a reduction in both the oxide growth and matrix contamination.
- (3) Relative humidity has a 0-12% effect on oxidation rate; the oxidation rate is higher in the presence of water vapor (humidity) in the air.
- (4) Grain size and microstructural variations in sheet and foil specimens have no measurable influence on the oxidation rate.
- (5) The oxygen solid solubility at the oxide-metal interface is (for the conditions investigated) significantly lower than the widely assumed value of 14.3 weight %. The observed solubilities for Ti-A55, Ti-6-2-4-2, and Ti-6-4 are 5, 3, and 3 weight %, respectively.
- (6) The depth of contamination is about 40  $\mu\text{m}$ , regardless of the alloy chemistry.
- (7) The fraction of oxygen partitioned into solid solution varies from 0.17 to 0.52 for the three alloys.
- (8) Microhardness measurement offers a simple and reliable technique for estimating the weight gain component due to matrix contamination.

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